

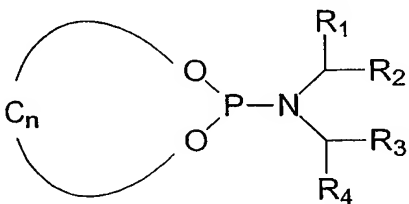
CLAIMS

WHAT IS CLAIMED IS:

1. A catalyst composition, comprising:
 (1) a catalyst precursor having the general structure
- $$MSX_n$$

wherein:

- M is a transition metal selected from the group consisting of iridium,
 molybdenum, and tungsten;
 S is a coordinating ligand;
 X is a counterion; and
 n is an integer from 0 to 5; and
 (2) a phosphoramidite ligand having the structure



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- wherein O-C_n-O is an aliphatic or aromatic diolate and wherein R₁, R₂, R₃, and R₄ are selected from the group consisting of substituted or unsubstituted aryl groups, substituted or unsubstituted heteroaryl groups, substituted or unsubstituted aliphatic groups, and combinations thereof, with the proviso that at least one of R₁, R₂, R₃, or R₄ must be a substituted or unsubstituted aryl or heteroaryl group.

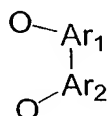
2. The catalyst composition of claim 1, wherein S is selected from the group consisting of ethylene, maleic anhydride, 1,5-cyclooctadiene, cyclooctene, 1,3-butadiene, 2,5-norbornadiene, benzene, hexamethyl benzene, cymene, cumene, cyclopentadiene, pentamethylcyclopentadiene, 1,2-diaminoethane, (R,R)-1,2 cyclohexanediamine, (S,S)-1,2-diphenyl-1,2-diaminoethane, (S,S)-1,2-dicyclohexyl-1,2-diaminoethane, and (S)-1,1'-bis-(p-methoxyphenyl)-1,2-propanediamine, and combinations thereof.

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3. The catalyst composition of claim 1, wherein X is selected from the group consisting of Cl, Br, I, acetate, BF₄, PF₆, ClO₄, p-toluene sulfonate, benzene phosphonate, tetra-pentafluorophenylborate, Li, Na, K, Mg, Ca, ammonium, alkyl-substituted ammonium., and combinations thereof.

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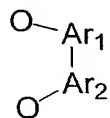
4. The catalyst composition of claim 1, wherein O-C_n-O is aromatic and has the structure



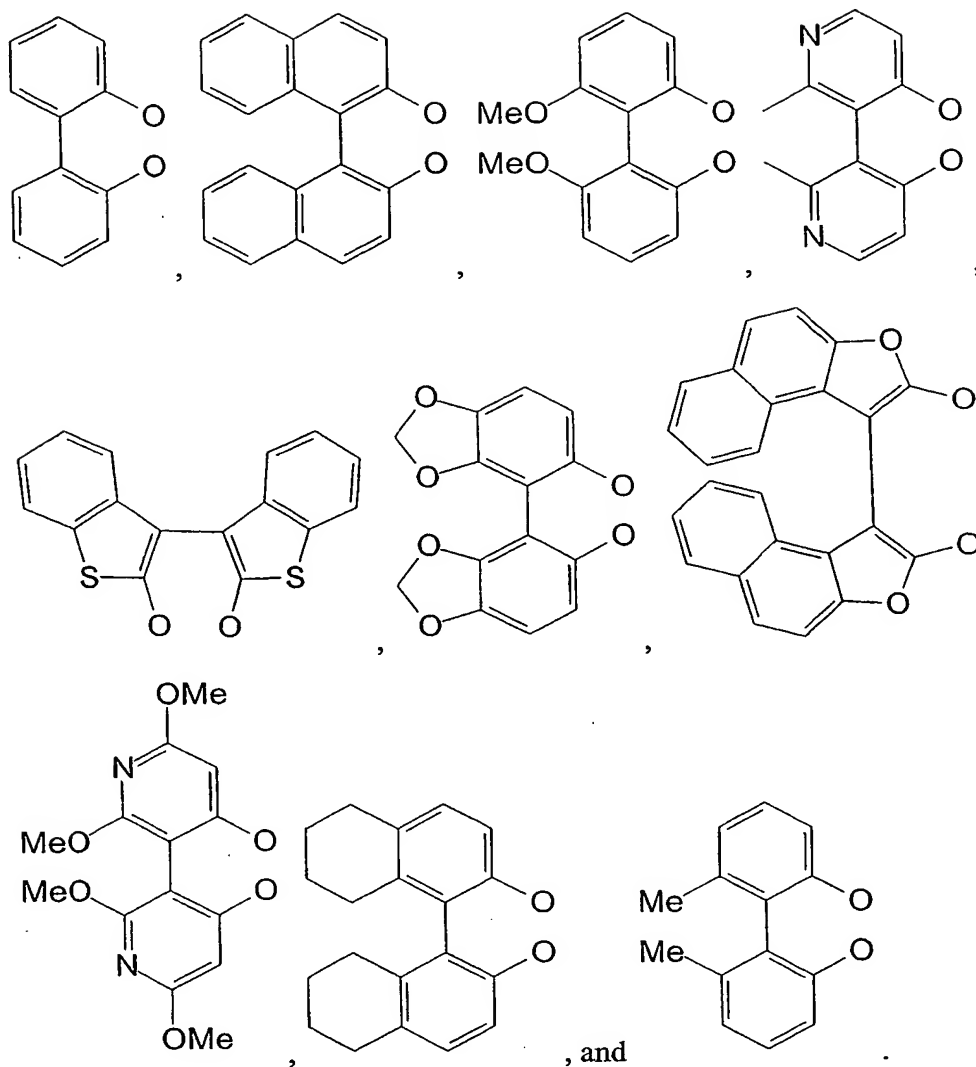
where Ar₁ and Ar₂ are individually aryl, substituted aryl, or heteroaryl.

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5. The catalyst composition of claim 4, wherein

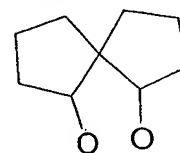


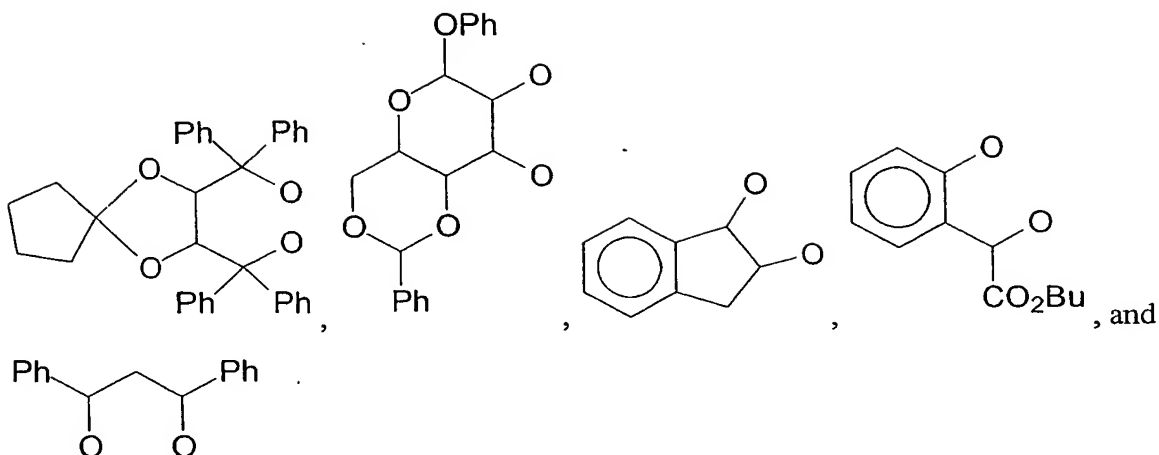
is selected from the group consisting of:



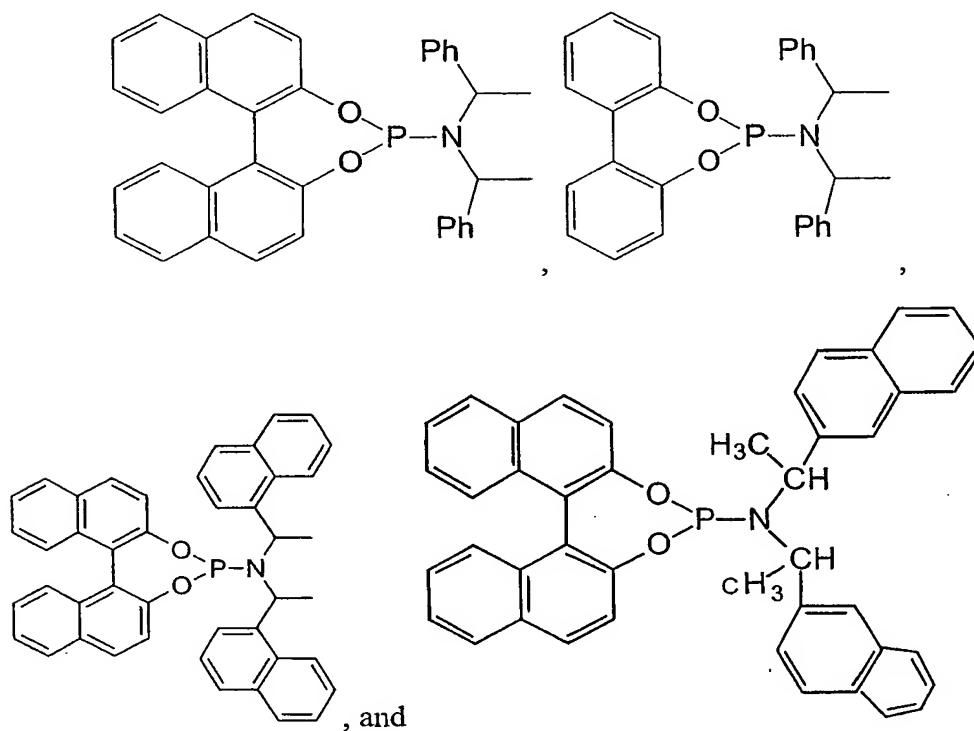
- 5 6. The catalyst composition of claim 1, wherein O-C_n-O is aliphatic and is selected

from 2,3-butanediol, 1,2-propanediol, 2-phenylene glycol,

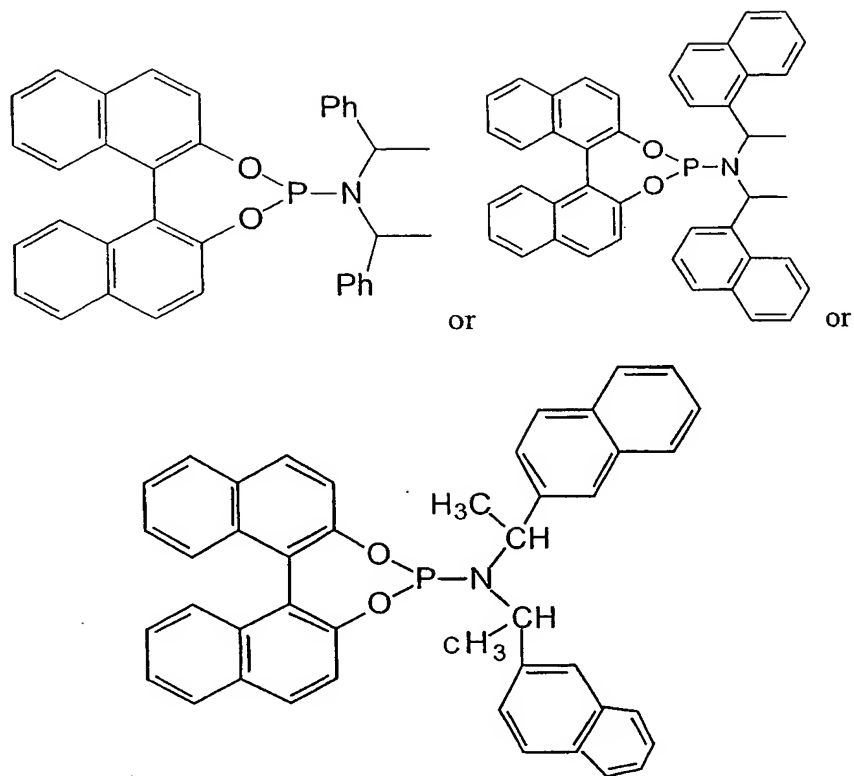




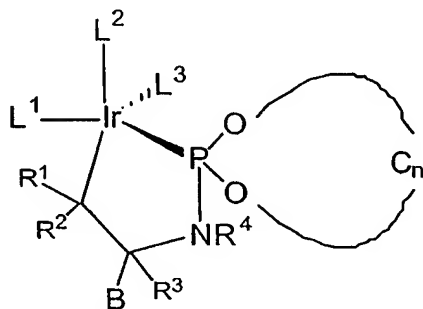
7. The catalyst composition of claim 1, wherein said phosphoramidite ligand has the
5 structure selected from the group consisting of



8. The catalyst composition of claim 1, wherein said catalyst precursor has the
10 structure
[(COD)IrCl]₂, wherein COD represents 1,5-cyclooctadiene, and said phosphoramidite
ligand has the structure



9. An activated catalyst, comprising a cyclometallated phosphoramidite having the
 5 structure



wherein:

O-C_n-O is an aliphatic or aromatic diolate;

B is any substituted or unsubstituted aryl or heteroaryl group;

- 10 R¹, R², R³, and R⁴ are independently selected from hydrogen, alkyl, benzylic and aromatic or heteroaromatic groups;

L¹ and L² are any ligands bound to Ir through an electron pair or through electrons in a pi-system of an unsaturated moiety; and

L^3 is an optional ligand selected from the group consisting of phosphine, phosphite, phosphoramidite, amine, heterocycle, carbon monoxide, and combinations thereof.

10. The activated catalyst of claim 9, wherein R^1 , R^2 , R^3 , and R^4 are independently selected from methyl, benzyl, phenethyl, diphenylmethyl, and phenyl.

11. The activated catalyst of claim 9, wherein L^1 and L^2 are independently selected from diolefins, monoolefins, diphosphines, monophosphines, diamines, monoamines, diheterocyclic units, and heterocyclic units.

12. A method of making an activated catalyst, said activated catalyst comprising a cyclometallated phosphoramidite, comprising the step of:

combining a catalyst precursor and a phosphoramidite ligand in the presence of a base under conditions that form said activated catalyst.

13. A method of preparing allylic amines enantioselectively, said method comprising the steps of:

reacting (a) an achiral or racemic allylic ester, allylic carbonate or allylic halide; (b) a reactant containing an N-H bond or a salt thereof, excluding lithium salts of N-benzyltosylamides; and (c) an optional additive selected from a base and a metal salt, said reacting step taking place in the presence of a solvent and a catalyst composition, said catalyst composition comprising a transition metal selected from the group consisting of iridium, rhodium, molybdenum, and tungsten, said reacting step taking place under conditions that enantioselectively form allylic amines.

14. A method of preparing allylic amines enantioselectively, said method comprising the steps of:

reacting (a) an achiral or racemic allylic ester, allylic carbonate or allylic halide; and (b)

a reactant containing an N-H bond or a salt thereof, in the presence of a solvent and a catalyst composition, said catalyst composition comprising:

(1) a catalyst precursor having the general structure



wherein:

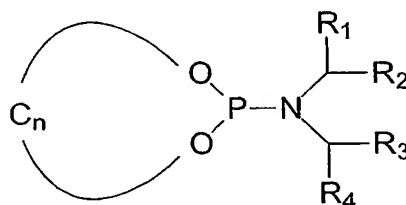
M is a transition metal selected from the group consisting of iridium, molybdenum, and tungsten;

S is a coordinating ligand;

X is a counterion; and

n is an integer from 0 to 5; and

(2) a phosphoramidite ligand having the structure



wherein O-C_n-O is an aliphatic or aromatic diolate and wherein R₁, R₂, R₃, and R₄ are selected from the group consisting of substituted or unsubstituted aryl groups, substituted or unsubstituted heteroaryl groups, substituted or unsubstituted aliphatic groups, and combinations thereof, with the proviso that at least one of R₁, R₂, R₃, or R₄ must be a substituted or unsubstituted aryl or heteroaryl group;

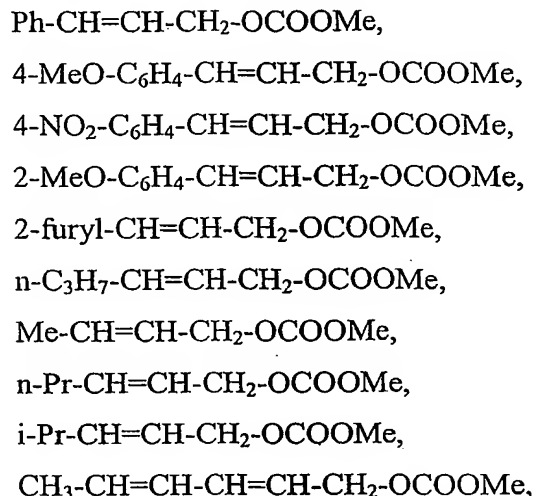
under conditions that enantioselectively form allylic amines.

15. The method of claim 14, wherein said achiral or racemic allylic ester is selected from the group consisting of

Ph-CH=CH-CH₂-OAc,
 4-MeO-C₆H₄-CH=CH-CH₂-OAc,
 4-NO₂-C₆H₄-CH=CH-CH₂-OAc,
 2-MeO-C₆H₄-CH=CH-CH₂-OAc,
 2-furyl-CH=CH-CH₂-OAc,
 n-C₃H₇-CH=CH-CH₂-OAc,
 Me-CH=CH-CH₂-OAc,
 n-Pr-CH=CH-CH₂-OAc,
 i-Pr-CH=CH-CH₂-OAc,
 CH₃-CH=CH-CH=CH-CH₂-OAc,

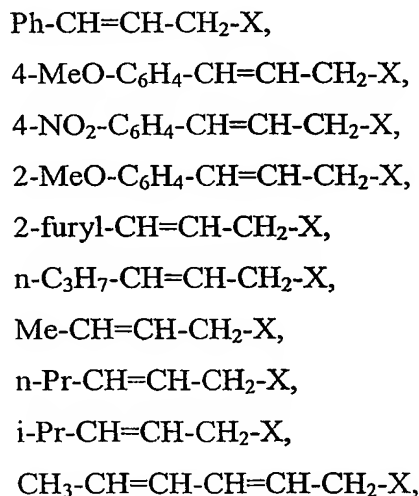
and combinations thereof.

16. The method of claim 14, wherein said achiral or racemic allylic carbonate is selected from the group consisting of



and combinations thereof.

17. The method of claim 14, wherein said achiral or racemic allylic halide is selected from the group consisting of:



and combinations thereof, wherein X is selected from the group consisting of F, Cl, Br, and I.

18. The method of claim 14, wherein said reactant containing an N-H bond, or salt thereof, is selected from the group consisting of ammonia, aromatic or aliphatic primary or

secondary amines, amides, carbamates, sulfonamides, imides, phosphoramides, imines, silylamines, heterocycles, and combinations thereof.

19. The method of claim 18, wherein said reactant containing an N-H bond, or salt thereof, is selected from the group consisting of substituted or unsubstituted anilines, diphenylmethanamine, benzylamines, 4-methoxybenzylamine; n-hexylamine, allyl amines; pyrrolidine, piperidine, morpholine; diethylamine; Boc_2NLi , LiN(CHO)_2 , benzophenone imine, tosylamide, and combinations thereof.

20. The method of claim 14, wherein said reacting step further takes place in the presence of an additional additive.

21. The method of claim 20, wherein said additional additive is a base selected from the group consisting of tertiary alkylamines, cyclic tertiaryamines, imines, and combinations thereof.

22. The method of claim 21, wherein said additional additive is selected from the group consisting of metal salts, metal halides, 1,4-diazabicyclo(2.2.2)octane (DABCO), and combinations thereof.

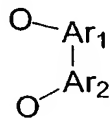
23. The method of claim 14, wherein said solvent is selected from the group consisting of DMF, ethanol, methanol, THF, acetonitrile, CH_3NO_2 , DME, CH_2Cl_2 , triethylamine, 1,4-dioxane, diethyl ether, toluene, hexane, and combinations thereof.

24. The method of claim 14, wherein S is selected from the group consisting of ethylene, maleic anhydride, 1,5-cyclooctadiene, cyclooctene, 1,3-butadiene, 2,5-norbornadiene, benzene, hexamethyl benzene, cymene, cumene, cyclopentadiene, pentamethylcyclopentadiene, 1,2-diaminoethane, (R,R)-1,2 cyclohexanediamine, (S,S)-1,2-diphenyl-1,2-diaminoethane, (S,S)-1,2-dicyclohexyl-1,2-diaminoethane, and (S)-1,1'-bis-(p-methoxyphenyl)-1,2-propanediamine, and combinations thereof.

25. The method of claim 14, wherein X is selected from the group consisting of Cl, Br, I, acetate, BF_4 , PF_6 , ClO_4 , p-toluene sulfonate, benzene phosphonate, tetra-

pentafluorophenylborate, Li, Na, K, Mg, Ca, ammonium, alkyl-substituted ammonium., and combinations thereof.

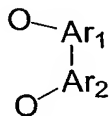
26. The method of claim 14, wherein O-C_n-O is aromatic and has the structure



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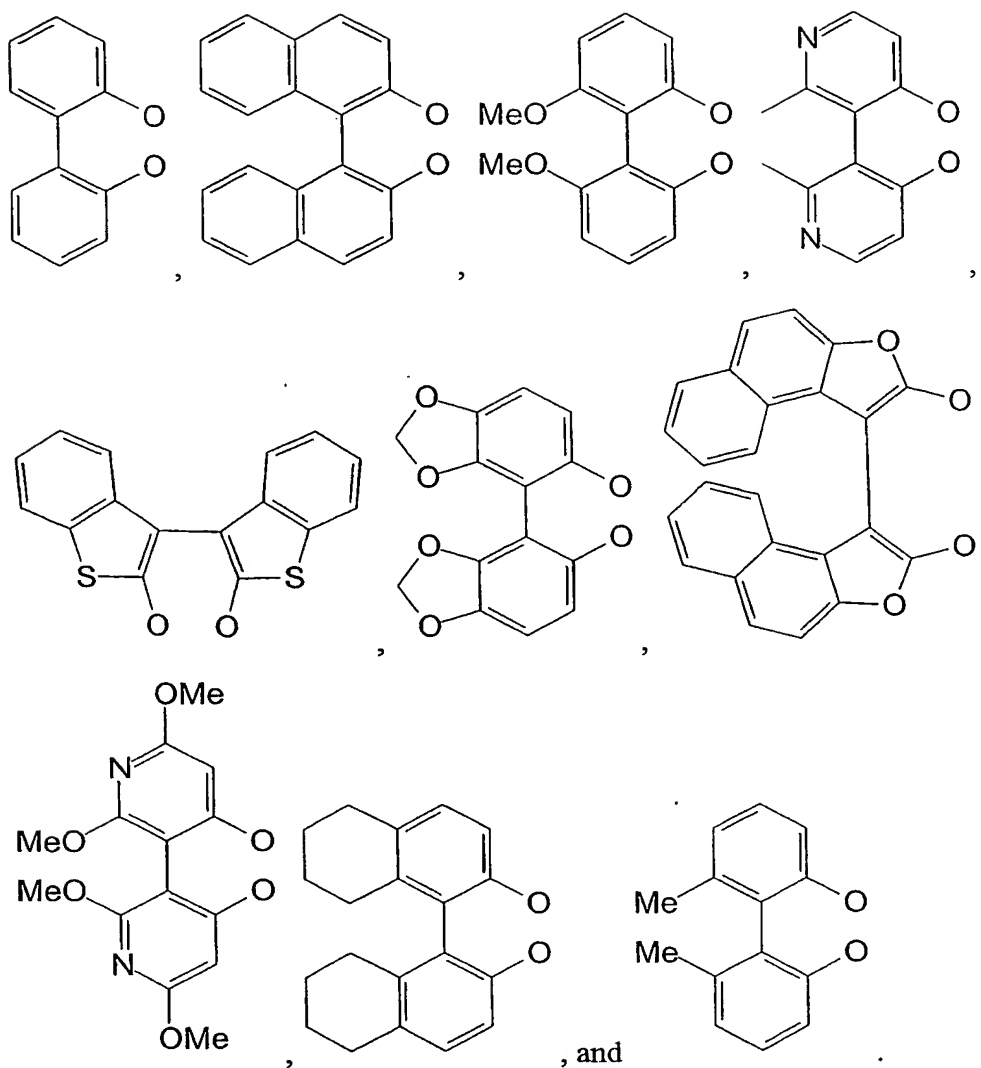
where Ar₁ and Ar₂ are individually aryl, substituted aryl, or heteroaryl.

27. The method of claim 26, wherein

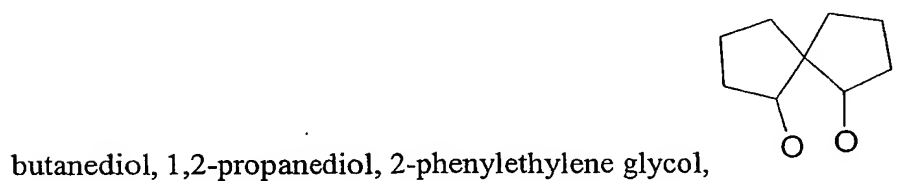


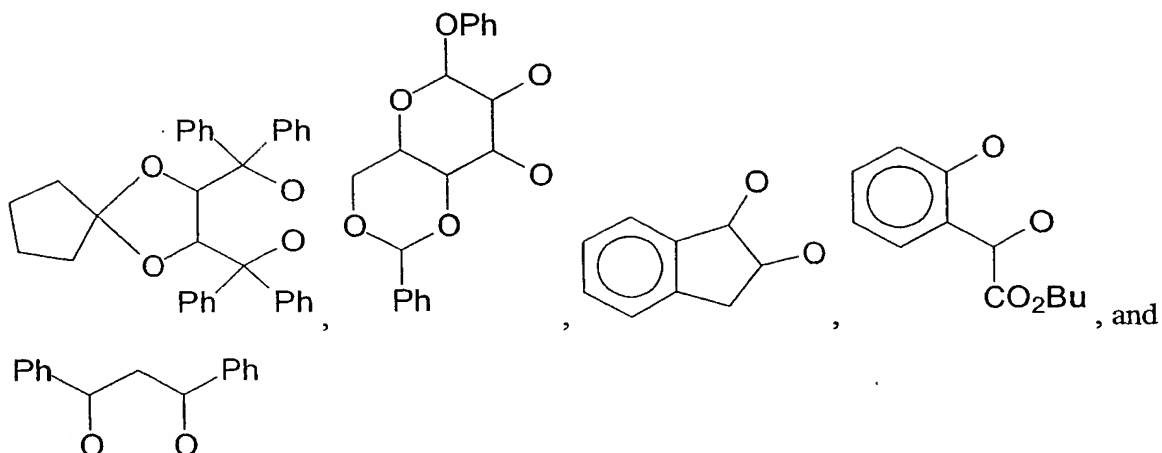
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is selected from the group consisting of:

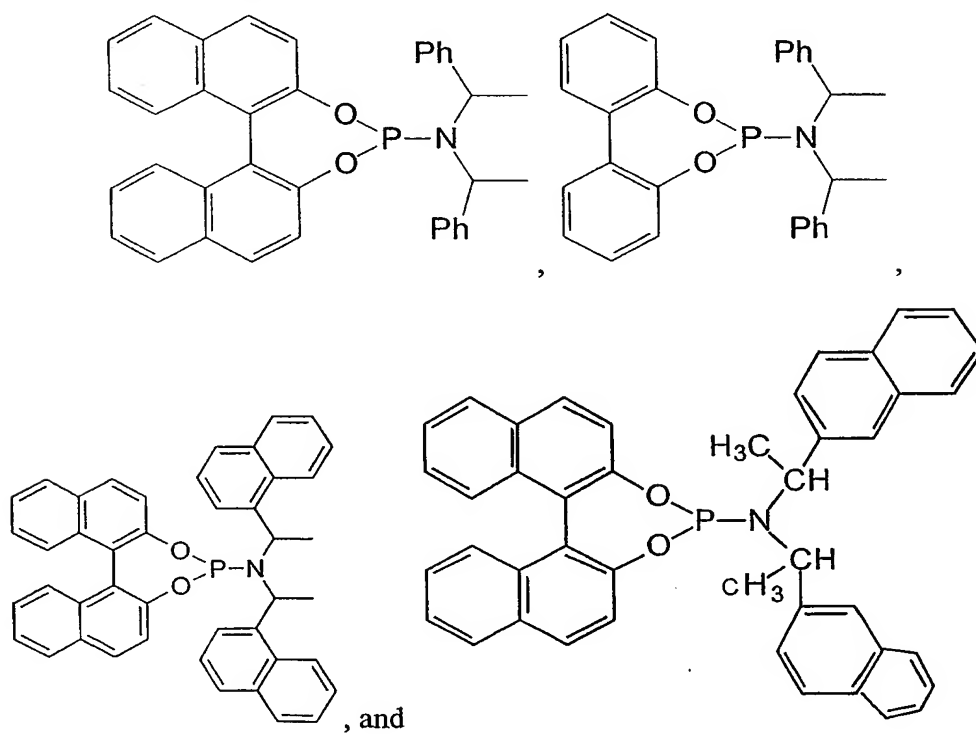


- 5 28. The method of claim 14, wherein O-C_n-O is aliphatic and is selected from 2,3-

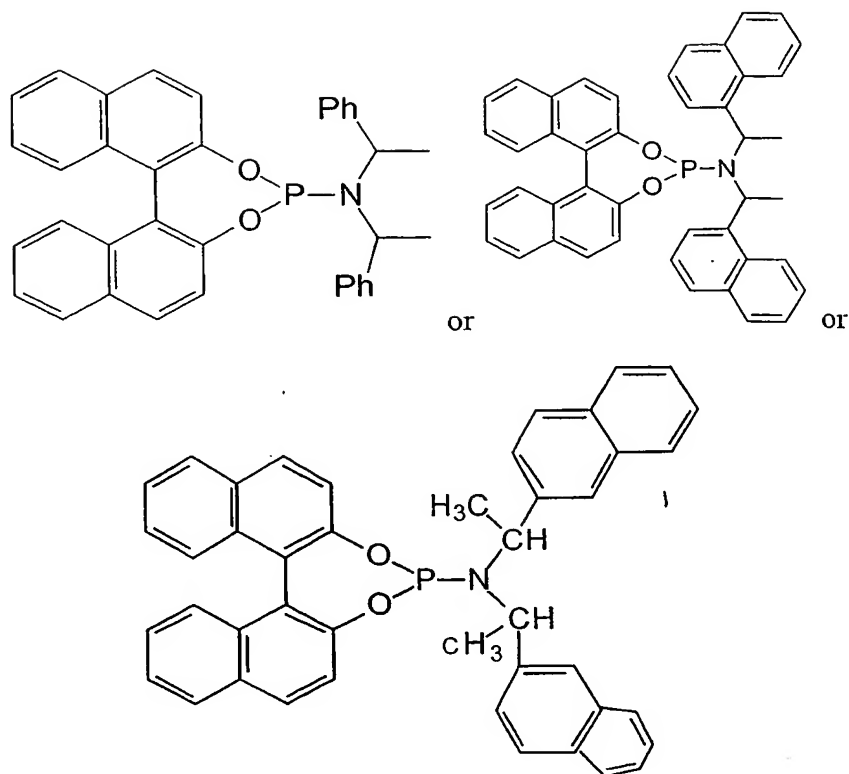




29. The method of claim 14, wherein said phosphoramidite ligand has the structure
5 selected from the group consisting of



30. The method of claim 14, wherein said catalyst precursor has the structure
10 $[(\text{COD})\text{IrCl}]_2$, wherein COD represents 1,5-cyclooctadiene, and said phosphoramidite
ligand has the structure



31. The method of claim 14, wherein said conditions comprise reaction temperatures ranging from 20 to 60°C, and reaction times ranging from 1 to 96 hours.
32. The method of claim 14, wherein the ratio of the amounts of said phosphoramidite ligand to said catalyst precursor is approximately 2:1.
33. The method of claim 14, wherein the enantiomeric excess (ee) of said method is greater than approximately 70%.
34. A method of preparing allylic ethers enantioselectively, said method comprising the steps of:
- reacting (a) an achiral or racemic allylic ester, allylic carbonate or allylic halide; (b) a reactant containing an O-H bond, and (c) optionally, a base; said reacting step taking place in a solvent and in the presence of a catalyst composition, said catalyst composition comprising a transition metal selected from the group consisting of iridium, rhodium,

ruthenium, molybdenum, and tungsten, said reacting step taking place under conditions that enantioselectively form allylic ethers.

35. A method of preparing allylic ethers enantioselectively, said method comprising the steps of:

reacting (a) an achiral or racemic allylic ester, allylic carbonate or allylic halide and (b) a reactant containing an O-H bond, or a salt thereof, said reacting step taking place in a solvent and in the presence of a catalyst composition, said catalyst composition comprising:

(1) a catalyst precursor having the general structure



wherein:

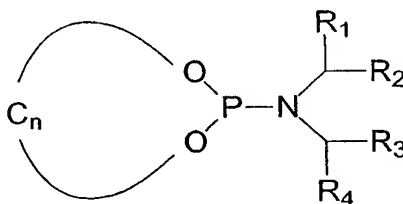
M is a transition metal selected from the group consisting of iridium, molybdenum, and tungsten;

S is a coordinating ligand;

X is a counterion; and

n is an integer from 0 to 5; and

(2) a phosphoramidite ligand having the structure



wherein O-C_n-O is an aliphatic or aromatic diolate and wherein R₁, R₂, R₃, and R₄ are selected from the group consisting of substituted or unsubstituted aryl groups, substituted or unsubstituted heteroaryl groups, substituted or unsubstituted aliphatic groups, and combinations thereof, with the proviso that at least one of R₁, R₂, R₃, or R₄ must be a substituted or unsubstituted aryl or heteroaryl group; under conditions that enantioselectively form allylic ethers.

36. The method of claim 35, wherein said achiral or racemic allylic ester is selected from the group consisting of

Ph-CH=CH-CH₂-OAc,
 4-MeO-C₆H₄-CH=CH-CH₂-OAc,
 4-NO₂-C₆H₄-CH=CH-CH₂-OAc,
 2-MeO-C₆H₄-CH=CH-CH₂-OAc,
 2-furyl-CH=CH-CH₂-OAc,
 n-C₃H₇-CH=CH-CH₂-OAc,
 Me-CH=CH-CH₂-OAc,
 n-Pr-CH=CH-CH₂-OAc,
 i-Pr-CH=CH-CH₂-OAc,
 CH₃-CH=CH-CH=CH-CH₂-OAc,

and combinations thereof.

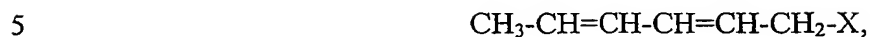
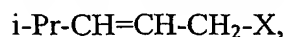
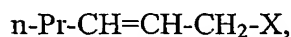
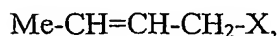
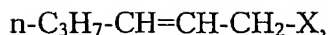
37. The method of claim 35, wherein said achiral or racemic allylic carbonate is selected from the group consisting of

Ph-CH=CH-CH₂-OCOOR₂,
 4-MeO-C₆H₄-CH=CH-CH₂-OCOOR₂,
 4-NO₂-C₆H₄-CH=CH-CH₂-OCOOR₂,
 2-MeO-C₆H₄-CH=CH-CH₂-OCOOR₂,
 2-furyl-CH=CH-CH₂-OCOOR₂,
 n-C₃H₇-CH=CH-CH₂-OCOOR₂,
 Me-CH=CH-CH₂-OCOOR₂,
 n-Pr-CH=CH-CH₂-OCOOR₂,
 i-Pr-CH=CH-CH₂-OCOOR₂,
 CH₃-CH=CH-CH=CH-CH₂-OCOOR₂,

and combinations thereof, wherein R₂ is a methyl or ethyl group.

38. The method of claim 35, wherein said achiral or racemic allylic halide is selected from the group consisting of:

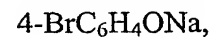
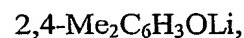
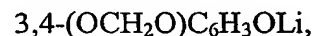
Ph-CH=CH-CH₂-X,
 4-MeO-C₆H₄-CH=CH-CH₂-X,
 4-NO₂-C₆H₄-CH=CH-CH₂-X,
 2-MeO-C₆H₄-CH=CH-CH₂-X,
 2-furyl-CH=CH-CH₂-X,



and combinations thereof, wherein X is selected from the group consisting of F, Cl, Br, and I.

39. The method of claim 35, wherein said reactant containing an O-H bond, or salt thereof, is selected from the group consisting of alkoxides, phenoxides, siloxides, carboxylates, phosphates, alcohols, phenols, silanols, carboxylic acids, phosphorus-containing acids, and combinations and salts thereof.

40. The method of claim 39, wherein said alkoxide or phenoxide is selected from the group consisting of



and combinations thereof.

41. The method of claim 35, wherein said reacting step further takes place in the presence of a base.

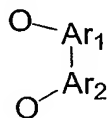
42. The method of claim 41, wherein said base is selected from the group consisting of 1,4-diazabicyclo(2.2.2)octane (DABCO), triethylamine, isopropyl-diethylamine, ethyl dimethylamine, metal hydrides, amides, alkoxides, carbonates, phosphates, and combinations thereof.

43. The method of claim 35, wherein said solvent is selected from the group consisting of DMF, ethanol, methanol, THF, acetonitrile, CH_3NO_2 , DME, CH_2Cl_2 , triethylamine, 1,4-dioxane, diethyl ether, toluene, hexane and combinations thereof.

44. The method of claim 35, wherein S is selected from the group consisting of ethylene, maleic anhydride, 1,5-cyclooctadiene, cyclooctene, 1,3-butadiene, 2,5-norbornadiene, benzene, hexamethyl benzene, cymene, cumene, cyclopentadiene, pentamethylcyclopentadiene, 1,2-diaminoethane, (R,R)-1,2-cyclohexanediamine, (S,S)-1,2-diphenyl-1,2-diaminoethane, (S,S)-1,2-dicyclohexyl-1,2-diaminoethane, and (S)-1,1'-bis-(p-methoxyphenyl)-1,2-propanediamine, and combinations thereof.

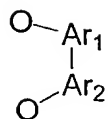
45. The method of claim 35, wherein X is selected from the group consisting of Cl, Br, I, acetate, BF_4 , PF_6 , ClO_4 , p-toluene sulfonate, benzene phosphonate, tetra-pentafluorophenylborate, Li, Na, K, Mg, Ca, ammonium, alkyl-substituted ammonium, and combinations thereof.

46. The method of claim 35, wherein $\text{O}-\text{C}_n-\text{O}$ is aromatic and has the structure

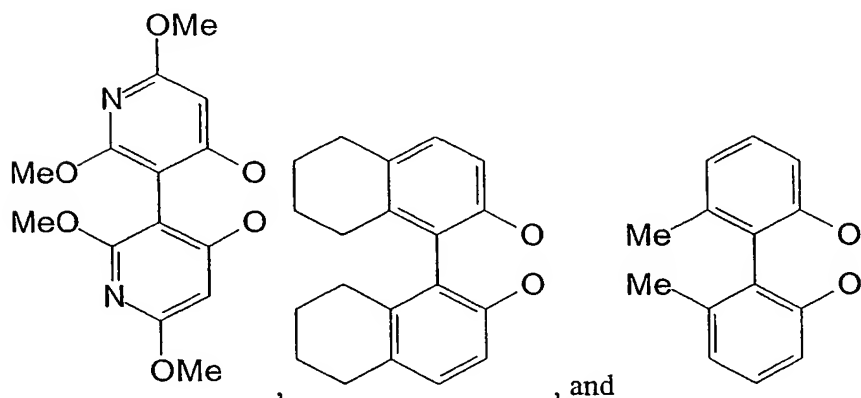
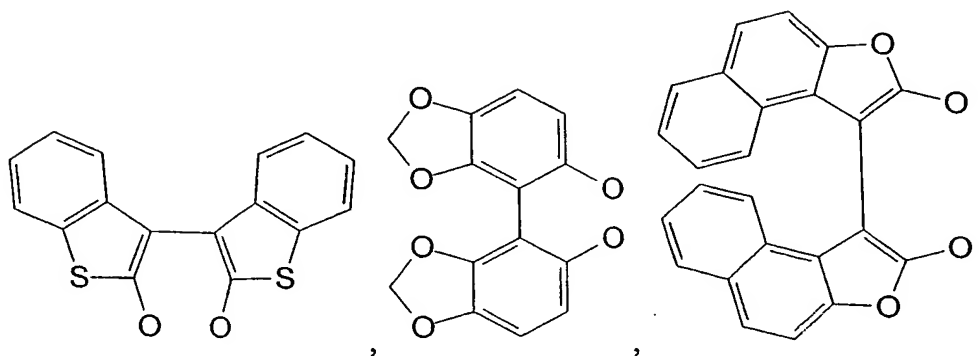
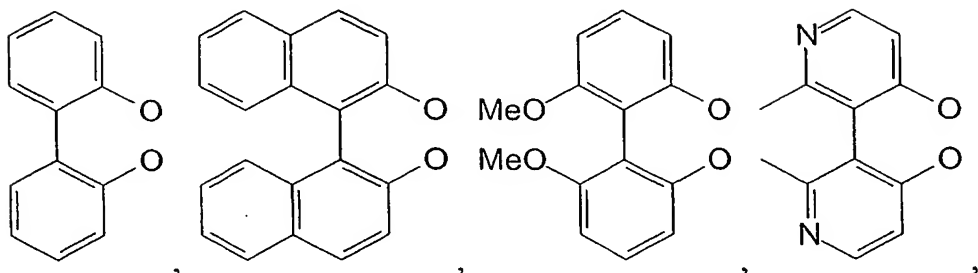


where Ar_1 and Ar_2 are individually aryl, substituted aryl, or heteroaryl.

47. The method of claim 46, wherein

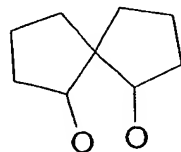


is selected from the group consisting of:

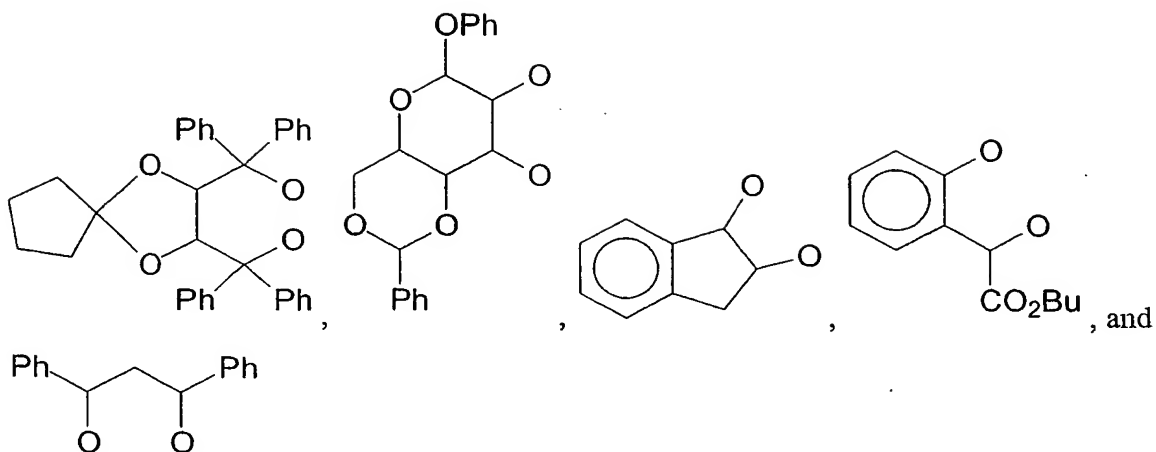


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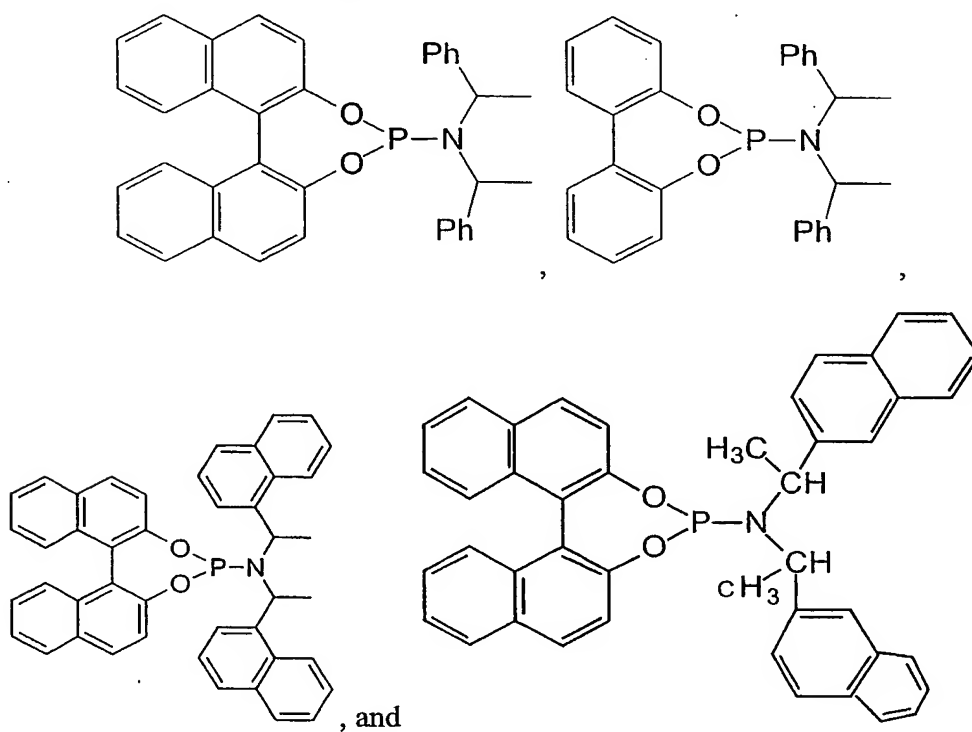
48. The method of claim 35, wherein O-C_n-O is aliphatic and is selected from 2,3-



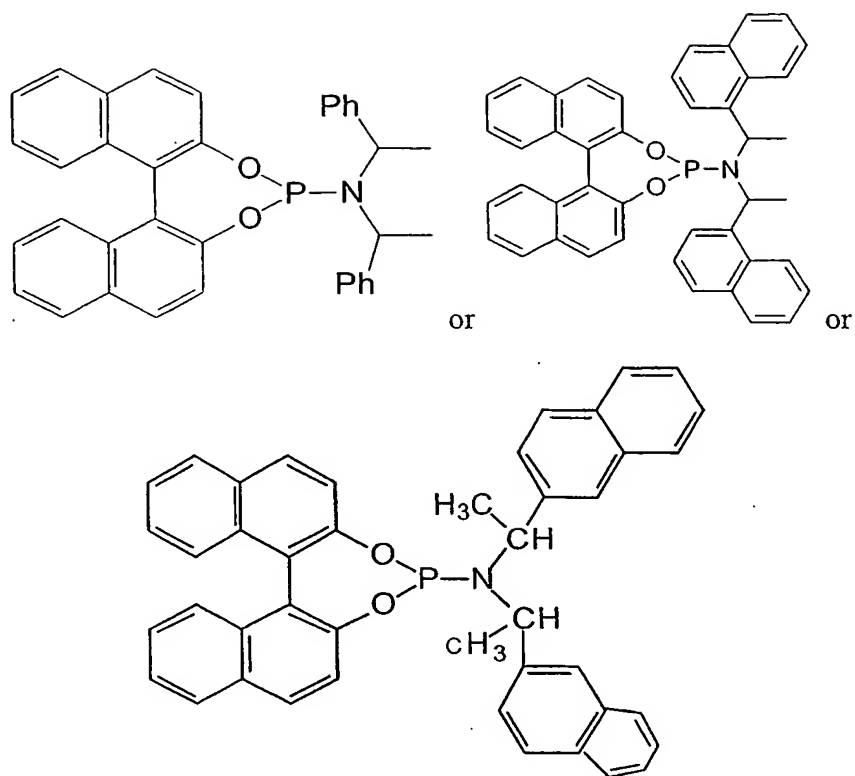
butanediol, 1,2-propanediol, 2-phenylethylene glycol,



49. The method of claim 35, wherein said phosphoramidite ligand has the structure
5 selected from the group consisting of



50. The method of claim 35, wherein said catalyst precursor has the structure
10 $[(\text{COD})\text{IrCl}]_2$, wherein COD represents 1,5-cyclooctadiene, and said phosphoramidite
ligand has the structure



51. The method of claim 35, wherein said conditions comprise reaction temperatures ranging from 20 to 60°C, and reaction times ranging from 1 to 96 hours.
52. The method of claim 35, wherein the ratio of the amounts of said phosphoramidite ligand to said catalyst precursor is approximately 2:1.
53. The method of claim 35, wherein the enantiomeric excess (ee) of said method is greater than approximately 70%.